



Hole storage overlayer of amorphous hafnium oxide for boosting hematite-based solar water splitting

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ABSTRACT

Hole storage layer (HSL) has been proved to be effective for constructing highly efficient photoelectrochemical (PEC) systems owing to its timely extraction and temporary storage of the photogenerated holes. Here we demonstrate an ultrathin HSL of amorphous hafnium oxide (HfO_x) by a combined strategy of hybrid microwave annealing (HMA) and in-situ Hf doping, which enhances the PEC performance collaboratively: i) in-situ doping of Hf⁴⁺ ions into hematite lattices to enhance the electrical conductivity in the bulk; and ii) amorphous HfO_x overlayer on hematite surface as a HSL to promote efficient charge separation between electrons and oxidizing equivalents in water oxidation. As a result, the fabricated Hf:Fe₂O₃@HfO_x nanorod photoanode achieves a photocurrent density of 3.47 mA cm⁻² at 1.23 V_{RHE} under simulated sunlight (100 mW cm⁻²). With NiCoFe(OH)_x co-catalyst modification, the photocurrent density further increases to 4.13 mA cm⁻² at 1.23 V_{RHE}, which is 3 times higher than that of bare hematite (1.24 mA cm⁻²) and comparable to the state-of-the-art hematite photoanode performance. This work demonstrates the high potential of the HMA-induced engineering of transition metal oxides applicable to the field of solar energy conversion.

1. Introduction

High solar-to-hydrogen (STH) conversion efficiency has been pursued persistently since the photoelectrochemical (PEC) water splitting into H₂ and O₂ was demonstrated with a TiO₂ photoelectrode in 1972 [1, 2]. Owing to earth abundance and intrinsic stability in aqueous solution, metal oxide semiconductors have been extensively studied as potential photoelectrode materials, such as WO₃, BiVO₄, Fe₂O₃, FeTi₂O₅ and Cu₂O [3–7]. Among them, hematite (α-Fe₂O₃) is considered an ideal candidate material because of its suitable band gap (~2.1 eV), non-toxicity, low cost, and good stability in alkaline solution [8,9]. However, hematite also suffers from a large onset potential (V_{on}), poor charge mobility (0.01–0.1 cm² S⁻¹ V⁻¹) [10], short hole diffusion distance (2–4 nm), and sluggish oxygen evolution reaction (OER) kinetics [11–13]. For these reasons, the achieved state-of-the-art STH conversion efficiency is still far below its theoretical value (~15.5 %) [14,15].

Generally, the PEC performance of hematite is severely limited by

the low separation efficiency of photogenerated electron-hole pairs at bulk as well as surface. The low intrinsic conductivity of hematite reduces the lifetime and diffusion length of charge carriers, which decreases the charge separation efficiency in the bulk. Furthermore, slow kinetics of water oxidation reaction influences the charge separation efficiency on the surface of the photoanode. In order to meet these challenges, various elaborate modification strategies have been implemented at different parts of the hematite photoanodes. Doping different high-valence ions (Sn⁴⁺, Ti⁴⁺, Nb⁵⁺, Ta⁵⁺, Ge⁴⁺) can increase the concentration and lifetime of charge carriers to improve electric conductivity in the bulk. This is an effective way to promote PEC performance, but it also has negative side effects by introducing defects and structural disorders [9,15–18]. Dhandole et al. reported that fluorine, zirconium co-doped hematite showed an improved PEC performance by promoting photogenerated electron transport in the bulk [19]. In particular, a surface hole-storage layer (HSL) has been proved to be an effective approach to promote hole extraction/separation, which increases the

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hole diffusion length to the surface and improves the separation efficiency of charge carriers [20–25]. Liu et al. demonstrated that a $\text{Ni}(\text{OH})_x$ hole-storage layer between Ta_3N_5 and coupled molecular catalysts restrained the charge recombination, leading to a photocurrent density (J_{ph}) of 12.1 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$ (close to the theoretical value of Ta_3N_5) [20].

Recently, hybrid microwave annealing (HMA) has been demonstrated to be a good alternative to conventional thermal annealing (CTA) in fabrication of highly efficient photoelectrodes by completing very high-temperature reactions in an extremely short time (a few minutes) [26], thus offering many distinctive advantages over CTA, such as maintaining the original morphology of nanostructures, making less damage to FTO, and inducing unconventional high-temperature reactions [7,27,28]. It should be noted that a reductive atmosphere is produced around the sample during the HMA process since graphite powder is used as a susceptor, which leads to the production of CO and CO_2 by partial combustion of the graphite. On the other hand, hafnium (Hf) has not been studied much as a dopant for hematite. A low concentration of Hf doping into hematite was proposed to be beneficial for formation of additional free electron polarons in the band structure according to a density functional theory (DFT) calculation [29]. Moreover, Hf doping from the surface could effectively reduce the diameter of hematite nanorods to increase the active surface area [30].

Here we report for the first time that hafnium engineering ameliorates hematite photoanodes in the bulk and surface. In detail, in-situ doping of Hf^{4+} ions into hematite lattices enhances the electrical conductivity in the bulk. Unexpectedly, the formation of an amorphous HfO_x layer on the hematite surface was found to become a HSL, which promoted surface charge separation effectively. This hole storage effect by an amorphous HfO_x layer for extracting/collecting photogenerated holes from hematite has never been reported before. Thus, the finally-engineered $\text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x$ photoanode exhibited a photocurrent density (J_{ph}) of 3.47 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$ under standard 1 sun condition. Additional $\text{NiCoFe}(\text{OH})_x$ co-catalyst modification further enhanced J_{ph} to 4.13 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$, which is 3 times higher than that of bare hematite (1.24 mA cm^{-2}).

2. Experimental methods

2.1. Fabrication of $\text{Hf:FeOOH}@ \text{HfOCl}_2$ on FTO

Several pieces of F-doped tin oxide glass (FTO, TEC8, 6–9 Ω , Pilkington) were ultrasonically cleaned by deionized water, ethanol, and acetone in sequence, which makes FTO surface sufficiently hydrophilic. Then, the FTO was immersed into a 25 mL aqueous solution of 1.0 g $\text{FeCl}_3 \cdot 6 \text{ H}_2\text{O}$ (Aladdin, 99.0 %), 2.1 g NaNO_3 (Aladdin, 99.0 %), 100 μL HNO_3 (Aladdin, 35.0 %), and an appropriate amount of HfCl_4 solution, and kept in an electric oven at 100°C for 2–3 h two times to obtain a yellow thin film of Hf:FeOOH nanorods on the FTO substrate. After completely rinsing by deionized water, the obtained Hf:FeOOH was spin-coated with different concentrations of HfCl_4 solutions to obtain $\text{Hf:FeOOH}@ \text{HfOCl}_2$.

2.2. HMA-synthesized core-shell structure of $\text{Hf:Fe}_2\text{O}_3 @ \text{HfO}_x$ photoanodes

Graphite powder (60 ~ 80 mL) was put in a Pyrex beaker (100 mL), which serves as a susceptor. The prepared sample was put on the slightly compacted graphite powder and treated in a home-made microwave oven (2.45 GHz, 1000 W) for 2–3 min at full power (100 %) to convert yellow $\text{Hf:FeOOH}@ \text{HfOCl}_2$ to red $\text{Hf:Fe}_2\text{O}_3 @ \text{HfO}_x$ photoanode.

2.3. Cocatalyst loading

For depositing $\text{NiCoFe}(\text{OH})_x$ as an OER catalyst on $\text{Hf:Fe}_2\text{O}_3 @ \text{HfO}_x$, the fabricated photoanodes were immersed into a $\text{NiCoFe}(\text{OH})_x$

precursor solution for 25 min at room temperature, which was prepared with 10 mM $\text{FeCl}_3 \cdot 6 \text{ H}_2\text{O}$, $\text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}$ (Aladdin, 99.0 %), and $\text{CoCl}_2 \cdot 6 \text{ H}_2\text{O}$ (Aladdin, 99.0 %).

2.4. Physical characterization

X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific spectrometer (K-Alpha) with $\text{Al K}\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, corresponding electron energy loss spectroscopy (EELS) mapping and linear scan were carried out on a Titan Themis Z machine (Thermo Fisher Scientific). Ultraviolet–visible absorbance spectra were measured on a UV-2700 spectrometer (Shimadzu). Scanning electron microscopy (SEM) images were obtained by ZEISS Gemini 300. The X-ray diffraction (XRD) spectra were measured on a Shimadzu XRD-6100, using $\text{Cu K}\alpha$ ($\lambda = 1.54056 \text{ \AA}$) radiation, an accelerating voltage of 40 kV, and an emission current of 30 mA.

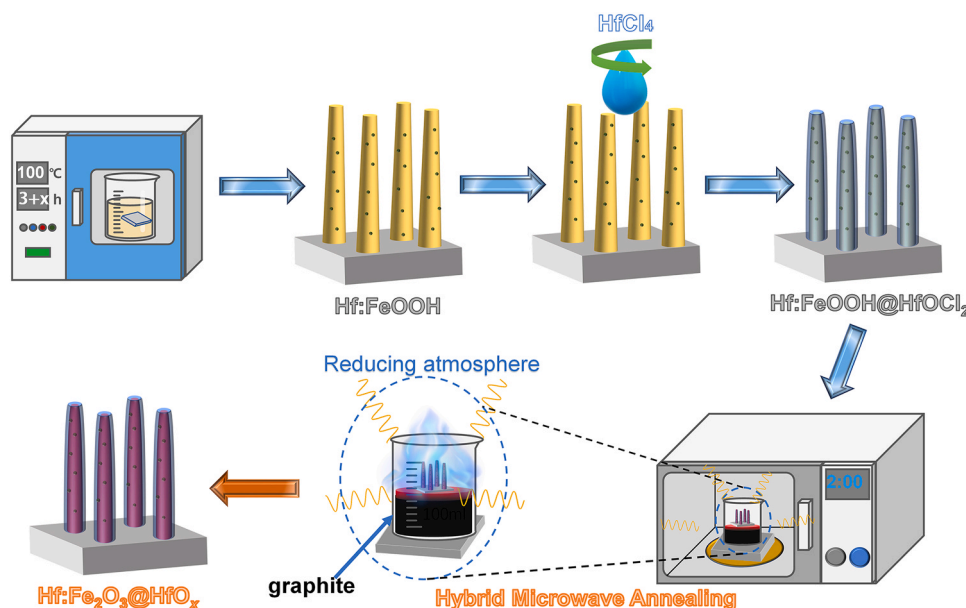
2.5. Photoelectrochemical measurements

The PEC performances were measured on a potentiostat (Iviumstat, Ivium Technologies) in a three-electrode system involving working electrode (the prepared photoanode with a 1 cm^2 illuminated area), reference electrode (Ag/AgCl , 3.0 M KCl solution), and counter electrode (Pt) in a 1.0 M NaOH solution as an electrolyte. J – V curves and photoelectrochemical impedance spectra (PEIS) were recorded under 1 sun (100 mW cm^{-2}) solar light generated by a solar simulator (Newport Sol 3 A with an AM 1.5 G filter), the intensity of which was calibrated with a standard silicon cell detector (Newport, PMKIT). All the measured potentials versus Ag/AgCl were converted to the potentials versus reversible hydrogen electrode using following equation: $E_{\text{RHE}} = E_{\text{Ag}/\text{AgCl}} + 0.059 \text{ pH} + E_{\text{Ag}/\text{AgCl}}^0$ ($E_{\text{Ag}/\text{AgCl}}^0 = 0.1976 \text{ at } 25^\circ\text{C}$). Linear sweep voltammetry (LSV) was measured in the range of 0.4 – $1.8 \text{ V}_{\text{RHE}}$ with a scan rate of 0.02 V s^{-1} . The Mott-Schottky plots were measured by sweeping 0.5 – $1.5 \text{ V}_{\text{RHE}}$ range with an alternative current (AC) frequency of 1000 Hz under the dark condition. The charge carrier density N_D was calculated by the equation: $(\frac{A_s}{C_{\text{bulk}}})^2 = \frac{2}{\epsilon\epsilon_0 e N_D} (V - E_{\text{FB}} - \frac{k_B T}{e})$, where $(\frac{A_s}{C_{\text{bulk}}})$ is the surface area-corrected space charge capacitance, ϵ_0 is the vacuum permittivity ($8.85 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$), ϵ is the dielectric constant of hematite (32), E_{FB} is the flat band potential, V is the applied voltage, e is electron charge ($1.602 \times 10^{-19} \text{ C}$), k_B is Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), T is the absolute temperature (298 K). PEIS spectra were recorded at $1.23 \text{ V}_{\text{RHE}}$ with an AC potential frequency range of 100,000–0.1 Hz. A Z-View software (Scribner Associates) was used to fit the experimental PEIS data to an equivalent circuit model. The incident photon-to-electron conversion efficiency (IPCE) was measured using a 300 W Xe lamp equipped with AM 1.5 G filter and a monochromator (Newport, CS260B) with a bandwidth of 10 nm at $1.23 \text{ V}_{\text{RHE}}$ in the same electrolyte. The incident photon-to-electron (IPCE) was calculated with the equation: $\text{IPCE} = \frac{1240 \times J(\text{mA/cm}^2)}{P_{\text{light}}(\text{mW/cm}^2) \times \lambda(\text{nm})}$, where J is the measured photocurrent density with a monochromator, P_{light} is the calibrated illumination power with a monochromator, and λ is the corresponding wavelength of the incident light.

3. Results and discussion

3.1. Fabrication and characterization of $\text{Hf:Fe}_2\text{O}_3 @ \text{HfO}_x$ nanorods

The fabrication process of $\text{Hf:Fe}_2\text{O}_3 @ \text{HfO}_x$ nanorod photoanode is depicted in Scheme 1. First, in-situ Hf-doped FeOOH (Hf:FeOOH) nanorods were grown on FTO by two consecutive steps of hydrothermal reaction to get a thick Hf:FeOOH film, which would improve the electronic conductivity of hematite by Hf^{4+} doping after conversion. Then, the HfCl_4 solution was spin-coated on Hf:FeOOH to form an amorphous HfOCl_2 layer. Subsequently, the prepared $\text{Hf:FeOOH}@ \text{HfOCl}_2$



Scheme 1. Schematic illustration for the synthesis of a Hf:Fe₂O₃ @HfO_x nanorod photoanode.

transformed into Hf:Fe₂O₃ @HfO_x by HMA, which accompanied a color change from yellow to dark red. Interestingly, the amorphous HfO_x layer formed on the nanorod surface displayed a hole storage capability instead of the well-known passivation effect as discussed below in detail. Note that the same HfCl₄ precursor solution was used for both modifications.

SEM images of the Hf:Fe₂O₃ film show the hematite nanorods of 650–800 nm long with diameters of 60–100 nm (Fig. S1), which are almost the same as the initial Hf:FeOOH nanorods before annealing (Fig. S2), confirming that HMA effectively maintained the original nanostructure. Besides, the surface of HMA-treated nanorods becomes smooth compared with Hf:FeOOH, suggesting that HMA not only converted Hf:FeOOH into Hf:Fe₂O₃ phase, but reconfigured the surface structure [31]. After construction of surface HfO_x overlayer, the diameters of Hf:Fe₂O₃ @HfO_x are almost the same as the ones without HfO_x overlayer (Fig. 1a; Fig. S1a), which demonstrates a very thin HfO_x overlayer. Moreover, the energy dispersive X-ray (EDX) mapping shows the uniform distribution of O, Fe, and Hf elements in the nanorod, and sum spectrum reveals the clear existence of Hf element (Fig. S3).

The atomic structure of Hf:Fe₂O₃ @HfO_x was further examined by STEM. The HAADF-STEM image in Fig. 1c clearly shows a core-shell structure of the nanorod made of a 1–3 nm amorphous HfO_x shell and a highly crystalline Hf:Fe₂O₃ core. The fast Fourier transforms (FFT) of two selected areas (Fig. S4) correspond to (110) plane of hematite with a *d*-spacing of 0.25 nm and (300) plane with a *d*-spacing of 0.15 nm, indicating that the significant incorporation of Hf atoms does not change the crystal structure of hematite, which is also supported by high resolution STEM in Fig. 1d. Many relatively larger bright points (dashed yellow circles) are observed clearly in hematite lattices, which are attributed to the substitutional Hf atoms. Besides, the EELS linear scanning (inset of Fig. 1d) clearly shows the high Hf concentrations in the shell and lower concentrations in the core with a modest gradient distribution, while Fe concentration displays exactly the reverse behavior. These results clearly verify the formation of Hf:Fe₂O₃ @HfO_x core-shell structure. In contrast, Hf:Fe₂O₃ shows a uniform distribution of Hf, Fe, and O elements in EELS mapping images (Fig. S5), indicating that Hf element was uniformly doped into hematite lattices. Due to a small optimal concentration of HfCl₄ and the limitation of spin-coating technique, there also exist some nanorods without HfO_x overlayer in Hf:Fe₂O₃ @HfO_x as shown in HAADF-STEM image in Fig. 1e, in which many bright points exist near the nanorod surface (within top ~3 nm

depth) ascribed to the substitutional Hf atoms [32,33]. These doped Hf atoms should have substituted into the Fe sites in (110) plane by HMA-induced rapid diffusion from the surface spin-coated HfCl₄. Moreover, the doped depth and area fluctuate at different surface locations, which is attributed to the fluctuation of local surface properties for the synthesized Hf:FeOOH nanorods. Our previous results demonstrated that the hydrophilic/hydrophobic surface (with/without oxygen plasma treatment) played an important role in the construction of shell structure during HMA [27,34]. The high-resolution STEM (HRSTEM) image shows a distinct feature of HAADF intensity, in which the bright points were identified as Hf atoms, while the light gray points in the background were ascribed to Fe atoms (Fig. 1f).

To further study local atomic arrangement of substitutional Hf atoms, a linescan for HAADF intensity was taken across the bright spots from surface to bulk, and the corresponding intensity data are plotted in the bottom of Fig. 1f. Clearly, the intensity of Hf atoms is much stronger than that of Fe atoms, and the average distance between two atoms is ~0.26 nm corresponding to the interatomic distance of Fe (110) plane [35], which in turn indicates that the substitution of Hf for Fe atoms does not change crystal lattices of hematite. Furthermore, the EELS mapping in Fig. 1g shows an inter-connected strong signal of Hf at the surface (white marked rectangle) relative to Fe and O signals, which is consistent with the ordered substitution of Hf for Fe atoms on the surface of nanorod (Fig. 1e). The blue marked area (inset of Fig. 1e) was transformed into inverse FFT image, which exhibits much clear difference between Hf and Fe atoms (Fig. 1h). Finally, the models of planar and three-dimensional structures are also constructed in Fig. 1i and j, respectively, which clearly display the atomic configuration of surface-doped structure.

The XRD patterns were used to analyze the crystallographic features of samples. Fig. 2a shows the similar XRD patterns with a strong peak intensity of (110) and weaker (104) and (012) peaks, which corresponds to the typical crystal structure of hematite (JCPDS no.33–0664) with no hafnium oxide impurity phases (HfO₂, FeHfO) [36]. Note that the half-width of (110) peak of Hf:Fe₂O₃ @HfO_x is a little larger than that of Hf:Fe₂O₃, implying that the HfO_x overlayer helps in maintaining a fine grain size of nanorods. More importantly, it has been proved that electron transport along (110) crystal plane is 4-orders of magnitude higher than that along (104) crystal plane [37]. In Fig. S6, the XRD of Hf:Fe₂O₃ @HfO_x prepared with 0.2 M HfCl₄ solution shows specific peaks representing rhombohedral α-Fe₂O₃ and monoclinic HfO₂ (JCPDS

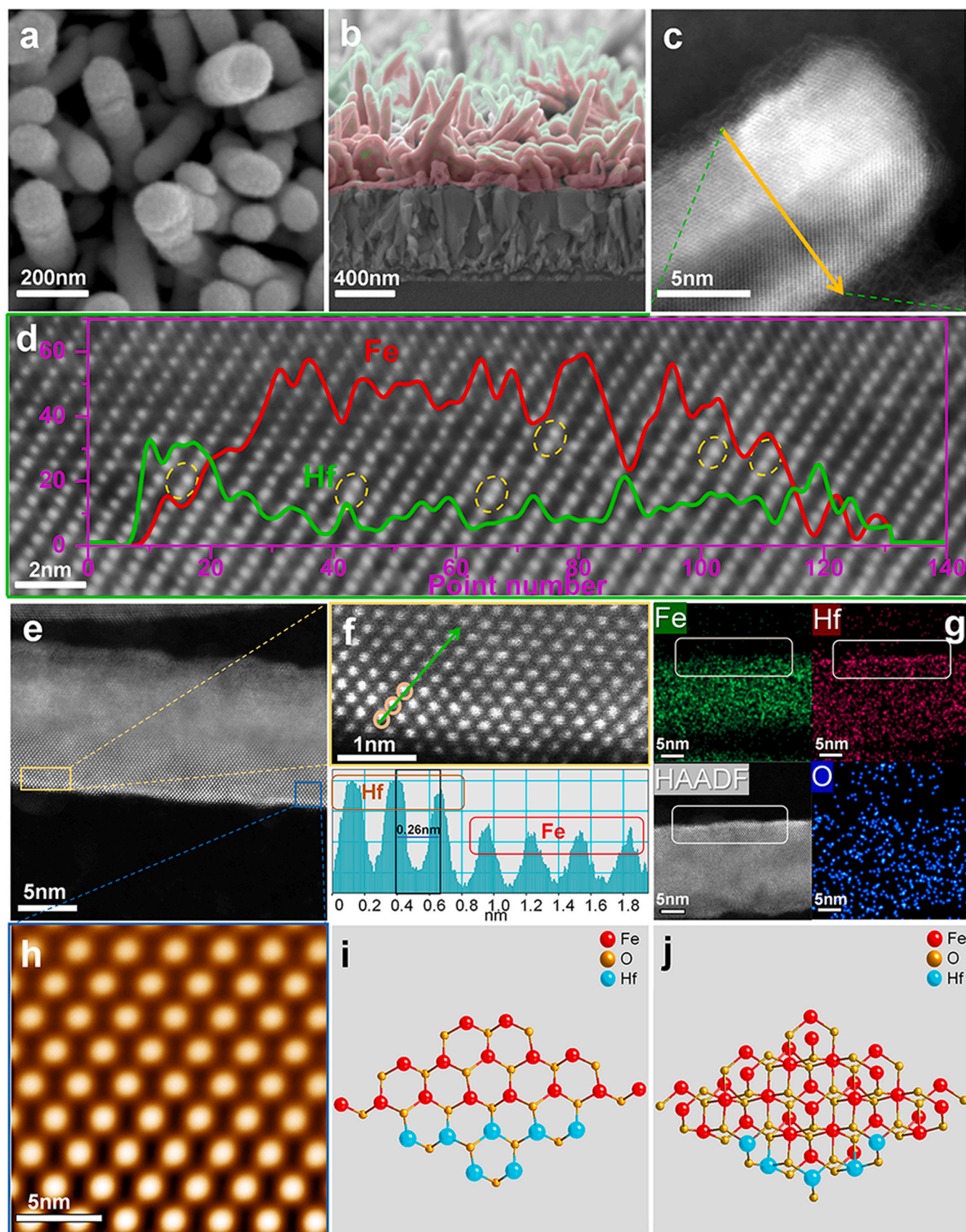


Fig. 1. Top and cross-section views of a, b) SEM, c) HAADF-STEM, d) HRSTEM (inset is the corresponding EELS linear scanning along the yellow arrow in (c) for Hf: Fe_2O_3 @ HfO_x core-shell nanorods. The images of e) HAADF-STEM, f) HRSTEM (green line-scan for HAADF intensity analysis), g) EELS-mapping, h) corresponding inverse FFT, and i, j) monolayer and three-dimensional model simulation for a heavily surface-doped nanorod in the sample of Hf: Fe_2O_3 @ HfO_x .

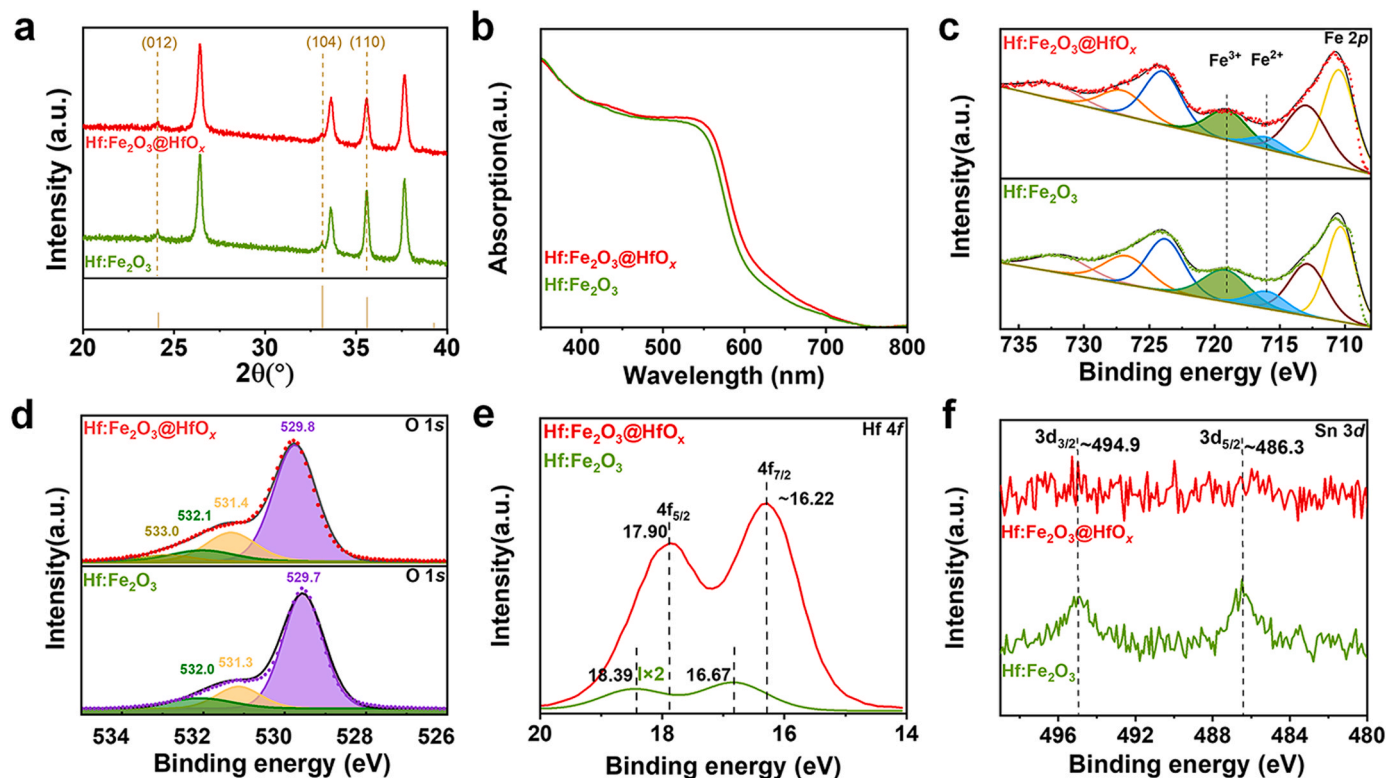


Fig. 2. (a) XRD patterns, (b) UV-vis absorption spectra, and XPS spectra of Hf:Fe₂O₃ and Hf:Fe₂O₃@HfO_x. (c) Fe 2p. (d) O 1s. (e) Hf 4f. (f) Sn 3d.

no.43–1017), indicating that the crystalline HfO₂ phase becomes visible as the concentration of HfCl₄ increases. However, the photocurrent density decreases rapidly with an increase of crystalline HfO₂ (Fig. S7). In contrast, when 0.05 M HfCl₄ was used, the complete absence of crystalline HfO₂ was observed, indicating it is in amorphous state, which is consistent with the above HRTEM result (Fig. 1c).

The UV-vis absorption spectra (Fig. 2b) were measured to evaluate the light harvesting capability. Hf:Fe₂O₃@HfO_x improves light absorption slightly relative to that of Hf:Fe₂O₃ owing to considerable substitution of Hf atoms (Fig. 1e, f) and external coating by the HfO_x overlayer (Fig. 1c). From the Tauc plots (Fig. S8), Hf:Fe₂O₃@HfO_x (~2.07 eV) shows a smaller bandgap relative to that of Hf:Fe₂O₃ (~2.09 eV), implying that more Hf dopants indeed decrease the band gap of hematite by generating impurity energy level.

The valence state and chemical composition of each element were examined by XPS (Fig. S9). The Fe 2p spectra in Fig. 2c can be deconvoluted into two main peaks with binding energies (BEs) of 724.08 eV and 710.28 eV corresponding to Fe 2p_{1/2} and 2p_{3/2} spin-orbit split peaks of Fe₂O₃, respectively [38]. The satellite peak at ~719 eV for the Fe³⁺ species is similar for both samples, while another weak satellite peak at ~716 eV for the Fe²⁺ species shows clear differences [34]. The Fe²⁺ satellite peak of Hf:Fe₂O₃@HfO_x becomes very weak owing to formation of the HfO_x overlayer, which protects hematite nanorods from losing oxygen atoms by reductive atmosphere of HMA.

The O 1s XPS spectra in Fig. 2d can be deconvoluted into three or four individual peaks corresponding to lattice oxygen (O_L, 529.7–530.2 eV), oxygen vacancy (O_V, 531.2–531.6 eV), and adsorbed oxygen/surface hydroxyl groups (O_{ad}/(OH)_{ad}, 532.0–533.0 eV) [39]. In fact, both HMA and Hf⁴⁺ ion doping could lead to O_V formation effectively. The substitution of Hf⁴⁺ for Fe³⁺ ions in hematite provides additional electron relocation and generates Fe²⁺ ions, which would accompany the formation of O_V for charge compensation [40]. Clearly, Hf:Fe₂O₃@HfO_x shows a higher O_V concentration compared to Hf:Fe₂O₃ due to the weaker Hf–O bonds of amorphous HfO_x overlayer. The results are consistent with the analysis of Fe²⁺ satellite peaks (Fig. 2c). It

should be noted that a proper concentration of O_V in hematite is beneficial for high PEC performance [41]. Moreover, O_{ad}/(OH)_{ad} signal can be observed notably in Hf:Fe₂O₃@HfO_x, and these hydrophilic groups tend to shift the location of surface states negatively to improve OER [42].

In Fig. 2e, Hf 4f XPS spectra of Hf:Fe₂O₃ show a doublet peak at ~16.67 eV and ~18.39 eV belonging to Hf 4f_{7/2} and Hf 4f_{5/2} orbitals of Hf(IV) state [27,28,43], which can improve the conductivity of hematite by donating additional electrons. In contrast, the BEs of those peaks in Hf:Fe₂O₃@HfO_x show a negative shift by ~0.4 eV to ~16.22 eV and ~17.90 eV with respect to that of Hf:Fe₂O₃, which indicates a lower oxidation state of Hf (<+4) in amorphous HfO_x shell. Undoubtedly, this behavior is related to the unique feature of reductive atmosphere induced by HMA, which leads to the generation of oxygen vacancies (O_V). The oxidation state of Fe could be reduced more easily in Hf:Fe₂O₃ to form Fe²⁺ ions since Hf–O bond is stronger than Fe–O bond [44]. In Hf:Fe₂O₃@HfO_x, however, HfO_x shell is exposed to the reducing atmosphere of HMA cell and is readily reduced, while Hf:Fe₂O₃ core would preserve oxygen atoms effectively due to protection by the HfO_x shell. These results are in agreement with Fe²⁺ satellite peaks (Fig. 2c) and generation of O_V (Fig. 2d). However, the substitutionally-doped Hf atoms on the surface still undergo reduction of Hf–O bonds due to the localized non-uniformity of the reductive atmosphere. Certainly, Hf:Fe₂O₃@HfO_x shows a higher Hf signal intensity owing to the HfO_x shell. It should be noted that a lower valence state of Hf in amorphous HfO_x shell is ready to extract and store the photo-generated holes from the core of Hf:Fe₂O₃ nanorods (discussed below).

Fig. 2f shows Sn 3d XPS peaks centered at ~486.3 eV (Sn 3d_{5/2}) and ~494.9 eV (Sn 3d_{3/2}) corresponding to BEs of SnO₂, indicating that Sn⁴⁺ ions were unintentionally doped into Hf:Fe₂O₃ nanorods from the FTO substrate during the process of HMA [16]. Obviously, Hf:Fe₂O₃ shows a weak Sn signal owing to Hf doping, while Sn signal disappears in Hf:Fe₂O₃@HfO_x due to significant additional obstruction of Sn diffusion by counter diffusion of Hf from the HfO_x shell.

3.2. Photoelectrochemical performance

The PEC water splitting performance of the prepared photoanodes was studied under simulated 1 sun irradiation (100 mW cm^{-2}) with an AM 1.5 G filter in 1 M NaOH electrolyte in a three-electrode cell with the photoanode, Ag/AgCl (3.0 M KCl), and Pt plate as working, reference, and counter electrodes, respectively (Fig. S10). Fig. 3a shows the photocurrent-potential (J - V) curves for hematite photoanodes with different modifications. The pristine $\alpha\text{-Fe}_2\text{O}_3$ photoanode showed a typical photo-response with a photocurrent density of 1.27 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$. The $\text{Hf:Fe}_2\text{O}_3$ photoanode was optimized with respect to the Hf dopant concentration (Fig. S11) and the condition of the double hydrothermal growth (re-growth) (Fig. S12), which thus generates a remarkable J_{ph} of 1.81 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$ under the standard conditions. With additional modification of HfO_x overlayer, J_{ph} is further enhanced to 3.47 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$ (Fig. S7), which is almost ~ 2 times that of the optimized $\text{Hf:Fe}_2\text{O}_3$. Besides, the J_{ph} reaches 5.53 mA cm^{-2} at $1.60 \text{ V}_{\text{RHE}}$, where the dark current begins to take off, indicative of a large fill factor. The performance is superior to the recently reported state-of-the-art hematite-based photoanodes without co-catalyst (Table S2). When CTA method was employed instead of HMA for the photoanode fabrication (Figs. S13 and S14), $\alpha\text{-Fe}_2\text{O}_3$ shows a modest J_{ph} of 0.93 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$ even though the same FeOOH precursor film was used for HMA. Both Hf doping and HfO_x overlayer show the expected promotional effects, making J_{ph} increase to 1.38 and 1.63 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$ sequentially, yet they are still less than a half of the performance of the corresponding photoanodes fabricated by HMA. The results highlight the superiority of HMA in fabricating high-efficiency photoelectrodes.

The onset potential (V_{on}) is another important figure of merit for photoanodes. It was evaluated by two ways (Fig. S15), both showing the similar values of 0.79, 0.87 and $0.85 \text{ V}_{\text{RHE}}$ for Fe_2O_3 , $\text{Hf:Fe}_2\text{O}_3$, and $\text{Hf:Fe}_2\text{O}_3@\text{HfO}_x$, respectively. Normally, doped metal ions form carrier

centers, which may increase the V_{on} of OER, while HfO_x overlayer shows a little decrease of V_{on} owing to the typical surface passivation effect. The E_{FB} and N_{D} were derived from Mott-Schottky plots (Fig. S16). Clearly, both Hf-doped photoanodes ($\text{Hf:Fe}_2\text{O}_3$, $\text{Hf:Fe}_2\text{O}_3@\text{HfO}_x$) show obvious decreases of the slope from that of bare hematite, indicating significant increases in donor densities [45]. Note that $\text{Hf:Fe}_2\text{O}_3@\text{HfO}_x$ shows an almost parallel slope with respect to that of $\text{Hf:Fe}_2\text{O}_3$, indicating that the HfO_x overlayer does not contribute much to increased N_{D} . It is against expectation because the HfO_x overlayer could provide additional Hf dopants to Fe_2O_3 . But protection by the HfO_x overlayer suppresses the formation of surface oxygen vacancy (O_V) in hematite (another source of charge carriers), which would offset the contribution from the HfO_x shell. Of course, the generated O_V in HfO_x overlayer itself by HMA would not contribute to the N_{D} of hematite. However, E_{FB} shows a difference of $\sim 100 \text{ mV}$ owing to generation of more surface states and O_V by Hf doping in $\text{Hf:Fe}_2\text{O}_3$ sample, while $\text{Hf:Fe}_2\text{O}_3@\text{HfO}_x$ shifts E_{FB} negatively because of the passivation effect and additional Hf doping at $1\sim 2 \text{ nm}$ depth of the hematite surface due to the HfO_x overlayer (Fig. 1e). These results are in agreement with the behavior of V_{on} (Fig. S15).

A most significant discovery of the current work is the hole-storage capability of the amorphous HfO_x overlayer. Transient photocurrent measurements under chopped illumination in Fig. 3b exhibit anodic/cathodic current spikes upon light on/off, which indicates that the photogenerated holes are accumulated at the photoanode|electrolyte interface, and would in turn take part in recombination with conduction band electrons [46,47]. Compared with the photoanodes without HfO_x overlayer, the $\text{Hf:Fe}_2\text{O}_3@\text{HfO}_x$ photoanode shows prominent current spikes at the potential range of $0.8\sim 1.3 \text{ V}_{\text{RHE}}$ both on light and in dark, suggesting that HfO_x overlayer serves the hole storage function. Thus, the HfO_x overlayer as a hole-storage layer could promote sluggish water oxidation kinetics, yet it can also lead to high possibility of recombination with conduction band electrons and back reaction (oxygen

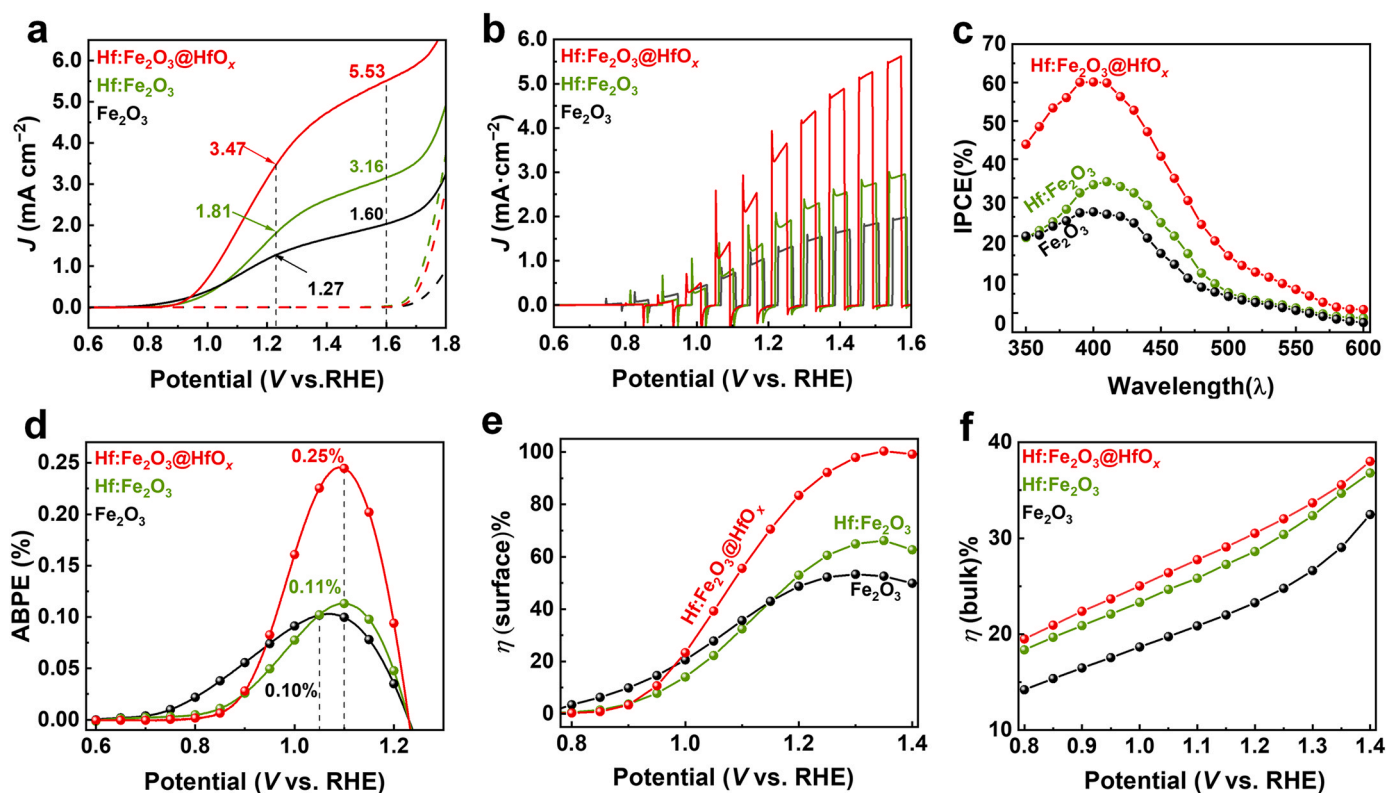


Fig. 3. Photoelectrochemical performance of Fe_2O_3 , $\text{Hf:Fe}_2\text{O}_3$, and $\text{Hf:Fe}_2\text{O}_3@\text{HfO}_x$ photoanodes a) J - V curves, b) chopped J - V curves, c) IPCE, d) ABPE, e) surface charge separation efficiency ($\eta(\text{surface})$), f) bulk charge separation efficiency ($\eta(\text{bulk})$).

reduction) owing to the extended lifetime of holes [48]. The latter negative effect can be mitigated by an effective OER co-catalyst as discussed later. Interestingly, HMA-treated $\text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x$ shows stronger anodic and cathodic current spikes from 0.8 V to 1.3 V_{RHE} in comparison with the same photoanode treated with CTA (Fig. S17a), indicating that HMA treatment could generate high hole-storage capability owing to its unique feature of reductive atmosphere. Besides, the surface charge separation efficiency (η_{surface}) of HMA-treated photoanode is substantially higher than that of CTA-treated photoanode (Fig. S17b), suggesting that the HfO_x overlayer formed by HMA could extract more efficiently the photogenerated holes from $\text{Hf:Fe}_2\text{O}_3$ nanorods and thereby promote the sluggish OER kinetics significantly using the accumulated/stored holes.

To explore the essential roles played by Hf doping and the HfO_x overlayer, PEIS was employed to study the charge transfer behaviors of prepared photoanodes. Representative two-RC-units equivalent circuit models were used to fit data obtained for Nyquist plots of Fe_2O_3 , $\text{Hf:Fe}_2\text{O}_3$, and $\text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x$ photoanodes (Fig. S18). The PEIS Nyquist plots were well-fitted using both circuit models and the detailed fitting values are listed in Table S3. The radii of semicircles (or the resistances) decrease gradually with additional modifications; $\text{Fe}_2\text{O}_3 > \text{Hf:Fe}_2\text{O}_3 > \text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x$. The charge transfer resistance (R_{ct}) of the $\text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x$ photoanode from the surface to electrolyte is significantly smaller than those of the others. However, its bulk resistance (R_{trap}) is commensurate with that of $\text{Hf:Fe}_2\text{O}_3$ owing to effective Hf doping for both photoanodes. On the other hand, the capacitance associated with surface states (C_{ss}) shows a large increase with decoration of HfO_x overlayer onto $\text{Hf:Fe}_2\text{O}_3$, which indicates that the extraction and storage capacity of photogenerated holes increases markedly [21].

The IPCE measured under 1 sun illumination (Fig. S19) is significantly enhanced by Hf doping and hole-storage layer (HSL) over the entire photon energy until it approaches zero at the band gap of hematite ($\lambda \sim 600$ nm). In particular, IPCE of $\text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x$ shows 15–25 % improvement relative to that of $\text{Hf:Fe}_2\text{O}_3$ in a wavelength range of 350–450 nm, indicating outstanding ability of solar photon conversion (Fig. 3c). Moreover, the integrated IPCE with reference to AM 1.5 G spectrum at 1.23 V_{RHE} gives a solar photocurrent (J_{SC}) of 1.27, 1.73, and 3.43 mA cm^{-2} for Fe_2O_3 , $\text{Hf:Fe}_2\text{O}_3$, and $\text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x$, respectively (Fig. S20), which are very close to the experimentally measured J_{ph} values at 1.23 V_{RHE} (Fig. 3a). Taken all these together, the enhanced IPCE by Hf doping and HfO_x overlayer is indeed due to the improved charge separation and hole-storage capability, respectively. The applied-bias photon-to-current conversion efficiency ($\text{ABPE} = J_{\text{ph}} \times (1.23 - E)/P_{\text{irradiation}}$) represents the net effect of photoelectrode by subtracting the contribution of bias potential (E). Fig. 3d shows increasing peak ABPE values in order of $\text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x$ (0.25 % at 1.10 V_{RHE}) $>$ $\text{Hf:Fe}_2\text{O}_3$ (0.11 % at 1.10 V_{RHE}) $>$ Fe_2O_3 (0.10 % at 1.05 V_{RHE}).

Bulk charge separation efficiency (η_{bulk}) and surface charge injection efficiency (η_{surface}) were determined in the same electrolyte with addition of 0.5 M H_2O_2 as a hole scavenger, as described in Fig. S21 [49]. The η_{bulk} denotes the fraction of photogenerated holes that reach the photoanode surface without recombination in the bulk of photoanode, while η_{surface} represents the fraction of those surface holes that are injected to the water oxidation successfully. In Fig. 3e, η_{surface} values are similar for Fe_2O_3 and $\text{Hf:Fe}_2\text{O}_3$, but $\text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x$ shows a greatly increased η_{surface} at potential range of 1.0–1.6 V_{RHE} owing to the efficient hole-storage capability of HfO_x layer. Interestingly, its η_{surface} value reaches near 100 % at ~ 1.3 V_{RHE} , indicating that the fraction of surface holes not yet participated in the reaction would be stored in the HfO_x layer temporarily instead of recombination with electrons, consequently making full use of holes that reached the surface, which is consistent with the previous reports [50,51]. In Fig. 3f, η_{bulk} of $\text{Hf:Fe}_2\text{O}_3$ shows a significant improvement relative to that of Fe_2O_3 starting from 0.8 V_{RHE} , indicating that Hf doping could effectively reduce bulk charge recombination by introduction of high valent ions [52,53]. However, the hole-storage layer of HfO_x improves η_{bulk} to a limited extent because the

electrical conductivity of hematite nanorods is already well-improved by initial in-situ Hf doping. It should be noted that the surface overlayer of HfO_x selectively extracts/stores photogenerated holes from the bulk of $\text{Hf:Fe}_2\text{O}_3$, thus significantly improving both bulk and surface charge separation efficiencies.

The capacity of hole storage can be quantified from the photocurrent response under chopped light illumination. By integrating the photocurrent transient peak, the amount of charge storage can be determined by the passed charges during the surface recombination process [54]. In Fig. S22, it is obvious that the quantity of holes stored in $\text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x$ increases with applied potential compared with $\text{Hf:Fe}_2\text{O}_3$ and Fe_2O_3 photoanodes (Fig. 4a), while the quantities show a little increase for $\text{Hf:Fe}_2\text{O}_3$ compared to Fe_2O_3 . Moreover, the HMA-treated $\text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x$ shows vastly higher hole-storage capacity than CTA-treated one (Fig. S23). All the above results demonstrate that HMA could form a more effective HfO_x hole-storage layer.

In order to verify whether the surface hole-extraction/storage layer can appear on all photoanodes, HfCl_4 solutions with different concentrations were spin-coated on the surface of pristine FeOOH nanorods directly. This is the usual procedure to prepare ex-situ doped hematite photoanodes. The optimized photoanode achieves an improved current density J_{ph} of 2.21 mA cm^{-2} at 1.23 V_{RHE} (Fig. S24a), but the current spikes of chopped J - V curves for pristine Fe_2O_3 and ex-situ Hf-doped Fe_2O_3 (ex- $\text{Hf:Fe}_2\text{O}_3$) are similar (Fig. S24b). The result suggests that the spin-coating of HfCl_4 solution on pristine FeOOH mainly results in Hf-doping instead of forming a hole-storage layer. This is further supported by the Mott-Schottky plot, which shows the doubled N_D of ex- $\text{Hf:Fe}_2\text{O}_3$ relative to that of pristine Fe_2O_3 (Fig. S24c). Note that N_D shows almost no increase from $\text{Hf:Fe}_2\text{O}_3$ to $\text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x$ (Fig. S16) as discussed before. The results demonstrate that only when the amount of pre-doped Hf is sufficient, the spin-coated Hf^{4+} ions could be effectively prevented from entering hematite lattices and instead form a thin amorphous HfO_x layer on the surface.

In addition to chopped-light J - V curves and PEIS, cathodic discharge measurements (CDM) can also be used to investigate the surface trapped holes [55,56]. In CDM sequence (detailed description in Fig. S25), the sample is first pre-oxidized by applying sufficient anodic bias (1.6 V_{RHE}) under illumination so as to drive water photo-oxidation and oxygen evolution. Then, the amount of charge stored in oxidized intermediates could be evaluated by the potentiodynamic discharge characteristics upon turning the light off by sweeping the potential cathodically [57]. The current responses of the photoanodes to the changes in illumination and potential conditions are shown in Fig. 4b. At a high intermediate potential (V_{int} , 1.3 V_{RHE}), the size of discharge wave for $\text{Hf:Fe}_2\text{O}_3$ indicates equivalent surface trapped holes or oxidized intermediates in the discharge time of 1.5–3.5 s. However, $\text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x$ in this period shows a relatively larger and delayed discharge wave, indicating that a larger amount of surface stored holes or oxidized intermediates take a longer time to reach the recombinational potential. At a middle V_{int} (1.0 V_{RHE}), the discharge wave appears in earlier period of 1.0–2.0 s, and the size follows the order of $\text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x > \text{Hf:Fe}_2\text{O}_3 > \text{Fe}_2\text{O}_3$, suggesting that HfO_x overlayer effectively influences the potentiodynamic discharge of oxidized intermediates. At a low V_{int} (0.8 V_{RHE}), the discharge waves of $\text{Hf:Fe}_2\text{O}_3$ disappear completely, while $\text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x$ still maintains a trace of discharge wave in the period of 0.9–1.5 s, indicating an outstanding hole-storage capability of HfO_x overlayer. Moreover, the capacitive spike of $\text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x$ in the period of 0.0–0.2 s is the largest, indicating the largest amount of discharged holes or oxidized intermediates (Fig. 4c). On the other hand, as the lower the applied potential is, the lower is the energy band bending towards the surface, consequently facilitating surface-trapped holes to combine with electrons. Definitely, the more driving force is required for $\text{Hf:Fe}_2\text{O}_3 @\text{HfO}_x$ to achieve a complete discharge of the stored holes (recombination with electrons) owing to the high hole storage capacity of the amorphous HfO_x overlayer.

In a 4 h stability test (Fig. 4d), Fe_2O_3 and $\text{Hf:Fe}_2\text{O}_3$ show the stability

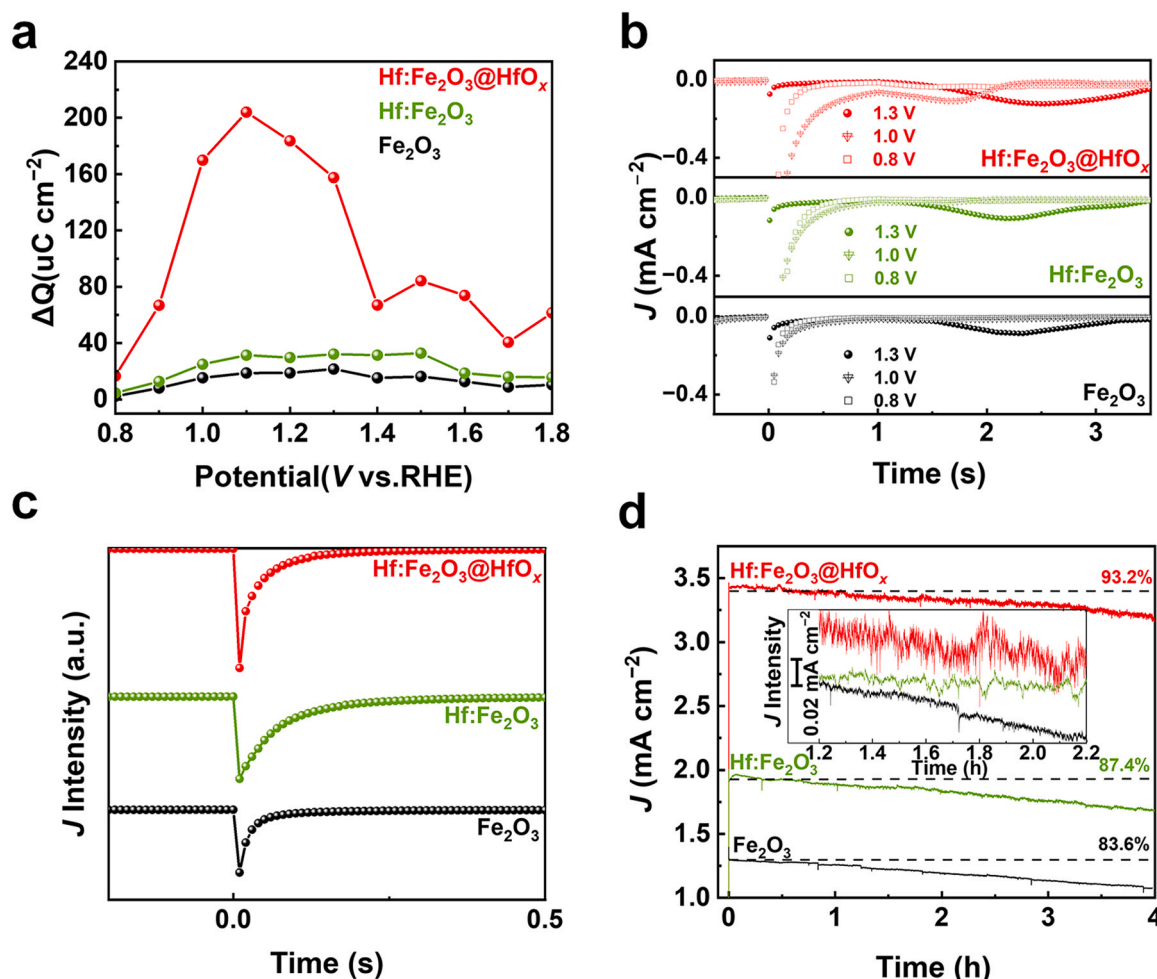


Fig. 4. Photoelectrochemical performance of Fe_2O_3 , $\text{Hf:Fe}_2\text{O}_3$, and $\text{Hf:Fe}_2\text{O}_3@\text{HfO}_x$ photoanodes; a) hole storage capacity, b) capacitive spike at 0.0–0.2 s with $V_{\text{int}} = 0.80 V_{\text{RHE}}$, c) cathodic discharge measurement, and d) stability test.

by losing ~16 % and ~13 % of the original photocurrents. However, $\text{Hf:Fe}_2\text{O}_3@\text{HfO}_x$ improves the stability by limiting photocurrent decay less than ~7 %, which results from surface protection capability of HfO_x overlayer by the large dissociation energy of $\text{Hf}-\text{O}$ bonds. In particular, the amplitude variation of photocurrent density for $\text{Hf:Fe}_2\text{O}_3@\text{HfO}_x$ is larger than those of Fe_2O_3 and $\text{Hf:Fe}_2\text{O}_3$ (inset of Fig. 4d), probably reflecting the dynamic processes of holes extraction, storage, and release in the HfO_x overlayer.

Although surface and bulk hafnium engineering brought markedly improved PEC performance of hematite photoanode, we applied an additional modification strategy. Thus, NiCoFe(OH)_x , a representative OER co-catalyst was deposited on the surface of $\text{Hf:Fe}_2\text{O}_3@\text{HfO}_x$ photoanode [58]. With NiCoFe(OH)_x loading under optimized conditions (Fig. S26), J_{ph} is further enhanced to 4.13 mA cm^{-2} at $1.23 V_{\text{RHE}}$ with cathodic shifting of V_{on} by 60 mV (Fig. S27a,b) [59]. Besides, the photocurrent spikes are obviously decreased with the co-catalyst (Fig. S27c), suggesting that NiCoFe(OH)_x can effectively transfer the holes stored in the HfO_x overlayer to participate in water oxidation, thus accelerating the slow kinetics of OER [9]. The results demonstrate a highly interesting and beneficial synergistic effect of a high hole storage/extraction capability of the HfO_x overlayer and fast injection of the holes into the electrolyte by the NiCoFe(OH)_x co-catalyst to promote efficient OER [22]. Moreover, the stability is further improved to 98.9 % in a 4 h test (Fig. S28d), which is significantly better than that of $\text{Hf:Fe}_2\text{O}_3@\text{HfO}_x$ (93.2 %).

4. Conclusions

We have demonstrated a distinctive strategy of HMA-induced hafnium engineering to boost the PEC performance of hematite, which involves two aspects of the bulk and surface: in-situ hafnium doping into the hematite lattice and the formation of amorphous HfO_x overlayer. In particular, HMA-induced amorphous HfO_x overlayer was found to display a distinctive function of hole storage, which promotes charge separation very efficiently. This effect by an amorphous HfO_x overlayer has never been reported before. The formation and functions of the hole-storage layer of amorphous HfO_x were unambiguously elucidated by multiple techniques, including HRTEM, chopped $J-V$ curves, PEIS, CDM, and near 100% η_{surface} . In contrast, CTA-treated hematite photoanode did not show the hole-storage function of HfO_x overlayer, and its J_{ph} was very low, which highlights the unique efficacy of HMA. Consequently, the fabricated $\text{Hf:Fe}_2\text{O}_3@\text{HfO}_x$ photoanode achieved a high J_{ph} of 3.47 mA cm^{-2} at $1.23 V_{\text{RHE}}$ under simulated 1-sun illumination. Moreover, NiCoFe(OH)_x cocatalyst modification demonstrated a synergistic promotional effect with the hole-storage function of HfO_x overlayer, recording J_{ph} of 4.13 mA cm^{-2} at $1.23 V_{\text{RHE}}$, which is 3 times higher than that of pristine Fe_2O_3 photoanode (1.24 mA cm^{-2}). The performance is comparable to the state-of-the-art hematite photoanodes reported recently.

Supporting Information

The [Supporting Information](#) is available free of charge on the website at Synthesized process scheme, surface morphologies of SEM images, EDX-SEM images, HRTEM images, XRD pattern, XPS survey spectra, J – V curves for optimization of HfCl_4 concentration and cocatalyst amount, J – V curves for bare hematite by HMA and CTA.

CRediT authorship contribution statement

Weicong Li: Conceptualization, Investigation, Writing - original draft. **Hongying Guo:** Investigation. **Chenyang Xu:** Validation, Formal analysis. **Chenke Tang:** Data curation, Software. **Jae Sung Lee:** Writing – review and editing. **Hemin Zhang:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123465](https://doi.org/10.1016/j.apcatb.2023.123465).

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